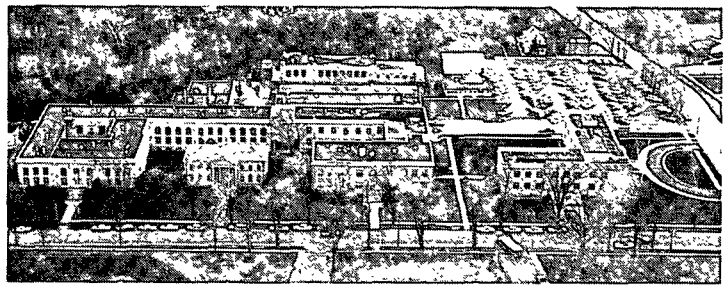

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THIOSULFATE EFFECTS ON CORROSION IN KRAFT WHITE LIQUOR

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ABSTRACT

The kraft pulping process uses an alkaline sulfide liquor known as white liquor to dissolve lignin from wood chips in the manufacture of pulp. White liquor is corrosive to carbon steel equipment used in liquor preparation and storage. Thiosulfate ions which are usually present in white liquor accelerate corrosion rates substantially. Coupon tests have been conducted to characterize the effect of thiosulfate on white liquor corrosivity toward carbon steel. Electrochemical tests were conducted to examine the origins of the corrosion acceleration that was observed. Accelerated corrosion was attributed to the occurrence of alternative cathodic reactions involving direct reduction of thiosulfate ions.

INTRODUCTION

The kraft pulping process utilizes an alkaline sulfide liquor to digest wood chips in the manufacture of chemical pulp. This alkaline sulfide solution, known as white liquor, typically contains 70-150 g/L NaOH, 20-50 g/L Na_2S, 10-60 g/L Na_2CO_3, and lesser amounts of NaCl, Na_2SO_3, $Na_2S_2O_3$, Na_2SO_4, and Na_2S_x (i.e., polysulfide).[1]

White liquor is prepared by dissolving the salt discharged from the chemical recovery boiler and recausticizing by contact with slaked lime. The chemical recovery boiler burns spent cooking liquors that have been concentrated by evaporation. The inorganic salts that remain after combustion of the organic species are recovered from the bottom of the boiler and dissolved in water to make green liquor. Green liquor is essentially a sodium carbonate, sodium sulfide solution. This green liquor is converted into white liquor by contact with slaked lime, which converts sodium carbonate to sodium hydroxide, with precipitation of calcium carbonates. The calcium carbonate precipitates are captured and are fired in a kiln to make lime that is reused for slaking. This entire process for production of white liquor is known as recausticizing.

Severe corrosion is often encountered on the plain carbon steel process equipment used in the recausticizing process. Carbon steel is the conventional material of construction of the clarifiers, storage tanks and miscellaneous recausticizing equipment. Uniform corrosion and pitting are often found on the steel surfaces wetted by white liquors, particularly in the wet/dry zone where liquor level fluctuations occur. Stainless steel equipment is virtually immune to corrosion by kraft white liquors, but the added expense involved in stainless steel construction may not be justifiable.

Certain oxidized sulfur species present in white liquor are known to accelerate corrosion of steel. In particular, thiosulfates and polysulfides have been implicated as the principal corrosion activators in white liquor.[2-12] Sodium thiosulfate is not intentionally added to the white liquor, but is found as an impurity which arises from air oxidation of the sulfides. Apparently, this oxidation can occur as a result of contact with oxygen in the air or because of incomplete reduction of sulfoxy compounds in the recovery boiler.

Although considerable research has been devoted to investigations of the role of thiosulfate as a corrosion activator, the current understanding of the origins of the thiosulfate effect remains relatively primitive. Previous authors[10] have attributed the effect of thiosulfate to its ability to stabilize small amounts of polysulfide through the disproportionation reaction shown in Eqn. 1.

$$Na_2S + Na_2S_2O_3 \longrightarrow Na_2S_2 + Na_2SO_3 \quad (1)$$

Polysulfide is an oxidizing species which can accelerate corrosion in white liquors in a manner similar to the acceleration of corrosion of steel by oxygen dissolved in water. That is, polysulfide controls the rate of corrosion through its contribution to the cathodic reduction process. Thiosulfate effects on corrosion were, in turn, attributed to the formation of a steady supply of polysulfide via the reaction in Eqn, 1.

However, the polysulfide interpretation of the thiosulfate effect is not supported by some of the available evidence. For example, the peak passivating current density for carbon steel exposed in simulated white liquors is found to increase, rather than decrase, when thiosulfates are present in the liquor.[9] If the effect of thiosulfate on white liquor corrosivity was simply an introduction of an oxidant, the applied current required to passivate steel should decrease. Reduction of the oxidizing species should assist in passivation by reducing the applied current density required to surmount the peak passivating current density. Furthermore, the addition of large amounts of thiosulfate does not initiate passivation of steel surfaces,[2] as might be expected with high concentrations of an oxidizing species. Thiosulfates also increase the corrosion of steel in liquors which contain no sodium sulfide, wherein the reaction in Eqn. 1 is impossible. Finally, cathodic polarization of a noble metal substrate reveals a diffusion-limited reduction rate attributed to polysulfide reduction,[14] but this limiting rate is insufficient to explain the high rate of corrosion encountered in thiosulfate-doped liquors.

These contradictions suggested that additional work was needed to elucidate the role of thiosulfate in the accelerated corrosion of carbon steel exposed to white liquor. Weight loss tests, electrochemical investigations, and analytical chemistry tests were employed to characterize the effect of thiosulfate on white liquor corrosivity and to examine the origins of the observed effects.

EXPERIMENTAL PROCEDURE

Solution Preparation

Synthetic white liquors were prepared for this study by adding reagent grade NaOH and $Na_2S.9H_2O$ crystals to deaerated water to produce a reference solution containing 100 g/L NaOH and 35 g/L Na2S. Anhydrous sodium thiosulfate

was added to create solutions containing 0, 2, 4, 6, 8, 10, 12, 16, 20 or 25 g/L $Na_2S_2O_3$. Because of concern over inadvertent introduction of sulfoxy compounds with the sulfide crystals, an additional test solution was prepared by bubbling pure H_2S gas through an NaOH solution until the NaOH and Na_2S concentrations were 100 and 35 g/L, respectively. However, subsequent chemical analysis indicated that this elaborate procedure did not significantly reduce the sulfoxy compound concentration in the resultant liquor.

Liquors were analyzed by acidimetric titrations, gas chromatography, and ion chromatography to determine the actual compositions of the test solutions. NaOH and Na_2S concentrations were determined by acidimetric titrations (i.e., the "ABC Titration"). Polysulfides were determined using a sensitive gas chromatographic method, and ion chromatography was used to determine concentrations of sulfoxy compounds. Analyses were determined before, after, and in some cases during the corrosion testing described below. Some of the solutions were also analyzed using visible and ultraviolet spectroscopy to observe possible complex formation.

Electrochemical Testing

Anodic and cathodic polarization scans were performed on carbon steel (type 1018) electrodes to observe the polarization behavior in each of the synthetic liquors. Scan rates of 1 mV/sec were used. The potentials were adjusted to compensate for IR losses in the electrolyte. A Type 304 stainless steel counter electrode was employed. The reference electrode used was the silver/silver-sulfide electrode whose reference potential in liquors containing 35 g/L of Na_2S is approximately -900 mVSCE.[14]

Cathodic polarization scans were also made using gold electrodes to characterize reduction characteristics on nonreactive electrode surfaces. In these scans, gold foil with a surface area of 4 cm^2 was used as the working electrode. Scan conditions were identical to those used in cathodic polarization of carbon steel electrodes.

Corrosion Rate Measurements.

Average corrosion rates were determined during exposure to the simulated white liquors using cylindrical, type 1018 carbon steel electrodes (surface area 4.5 cm^2) polished to a 600 grit finish before exposure. The electrodes were exposed at 90 C in fluorocarbon test chambers coated with oxygen impermeable paint to minimize liquor oxidation during exposure. The chambers were arranged so rest potentials could be determined throughout the four-week exposure period. Potentials were determined relative to silver/silver-sulfide electrode (SSSE) potentials obtained from silver electrodes which were also immersed in the liquors. Transfer of liquors and/or specimens was completed in a nitrogen-filled glove bag to minimize oxidation of the synthetic liquors.

When the electrodes were removed from the liquors at the end of the four week exposure, the deposits on the coupons were removed by scraping and analyzed by x-ray diffraction. The remaining corrosion product was then carefully removed and the electrodes were weighed for determination of average corrosion rates.

RESULTS

Weight Loss Tests — Corrosion Rates, Potentials and Deposit Analysis

In general, the average corrosion rate increased with increasing thiosulfate concentration, as did the electrode potential of the corrosion coupons. There were a few exceptions to this trend, however; for example, the highest corrosion rate was observed in a synthetic liquor containing 12 g/L thiosulfate. The results of the weight loss tests are summarized in Table 1 and plotted in Figure 1.

The rest potential of carbon steel electrodes immersed for several weeks was higher in synthetic liquors containing higher concentrations of thiosulfate. Rest potentials ranged from -230 to -30 mVSSSE, depending on liquor composition. Spontaneous passivation was not apparent at these elevated

two or three stable rest potentials were occasionally evident.

Cathodic curves generated on the nonreactive gold electrode exhibited two distinct regimes, as shown in Figure 4. At potentials slightly below the redox potential of gold, a diffusion-limited regime is observed which is attributed to the reaction

$$S_2^{-2} + 2e^- \longrightarrow 2S_2^- \qquad (2)$$

At potentials below -200 mVSSSE, a second cathodic reaction appears, which is attributed to the hydrogen reduction reaction

$$2H_2O + 2e^- \longrightarrow H_2(g) + 2OH^- \qquad (3)$$

The diffusion-limited current density associated with polysulfide reduction was slightly higher in liquors with higher levels of thiosulfate. Although this is consistent with the partial conversion of thiosulfate to polysulfide via reaction (1), the magnitude of the limiting current densities suggests that the extent of thiosulfate conversion to polysulfide is quite small. This is consistent with the equilibrium constant published[10] for reaction (1).

There was no evidence of direct thiosulfate reduction on the gold electrode, even though the half-cell potential for thiosulfate reduction lies well above the potentials achieved on the gold electrodes in cathodic scans. Apparently, the overvoltage associated with thiosulfate reduction is quite large and little thiosulfate reduction is encountered on inert noble metal electrodes at potentials in the vicinity of the typical carbon steel rest potentials.

When $NaFeS_2$ was present in the liquors, the diffusion-limited current density associated with the polysulfide reduction on the gold electrode decreased, compared to tests in solutions without $NaFeS_2$. Apparently, $NaFeS_2$ is not electroactive at potentials in the vicinity of the rest potential found on steel surfaces. Furthermore, the presence of $NaFeS_2$ does not appear to catalyze the polysulfide reaction presented in Equation 2.

DISCUSSION

Anodic Reactions

The dissolution reactions which are likely in the potential regime associated with corrosion of steel are elucidated by the anodic polarization curves and the recent treatment of the Fe-S-H_2O Pourbaix diagram by Crowe.[17] The peak at -150 mVSSSE, associated with the shoulder on a broad anodic peak, was attributed to the Fe/FeS oxidation reaction

$$Fe + HS^- \longrightarrow FeS + H^+ + 2e^- \qquad (4)$$

The corrosion coupons which exhibited FeS (actually, Fe_9S_8) as a surface corrosion product experienced corrosion rates on the order of 30 mpy. The mackinawite film apparently offers little protection against continued corrosion in this potential range.

At more noble potentials (Peak I in Figure 2), several reactions are thermodynamically possible, including

$$3Fe + 4H_2O \longrightarrow Fe_3O_4 + 8H^+ + 8e^- \qquad (5)$$

$$Fe + 3H_2O \longrightarrow Fe(OH)_3^- + 3H^+ + 2e^- \qquad (6)$$

$$3Fe(OH)_3^- + H^+ \longrightarrow Fe_3O_4 + 5H_2O + 2e^- \qquad (7)$$

The magnetite film is apparently much more protective than the iron sulfide films, which may explain the reduction in corrosion rates in the potential range, -215 to -125 mVSSSE. Although magnetite was not observed in diffraction analyses of corrosion deposits in this range, deposit sampling methods may have precluded such a finding. Care was taken to exclude surface films that were tightly adherent to the metal surface, so as not to jeopardize the

weight loss determination; tightly adherent magnetite would not have been sampled.

The anodic peak with the highest current density (Peak IA in Figure 2) could also be associated with several reactions. The reaction of FeS to form FeOOH, Fe_2O_3, or FeS_2 are all thermodynamically possible in this potential range

$$FeS + 2H_2O \longrightarrow FeOOH + HS^- + 2H^+ + e^- \quad (8)$$

$$2FeS + 3H_2O \longrightarrow Fe_2O_3 + 2HS^- + 4H^+ + 2e^- \quad (9)$$

$$FeS + HS^- \longrightarrow FeS_2 + H^+ + 2e^- \quad (10)$$

However, since substantial amounts of $NaFeS_2$ were found in corrosion deposits on specimens whose rest potentials remained in this regime, it is likely that FeS is oxidized only to FeS_2^- according to Equation (11)

$$FeS + HS^- + OH^- \longrightarrow FeS_2^- + H_2O + e^- \quad (11)$$

The potential for this reaction cannot be reported because of the absence of the necessary thermodynamic data. However, the potential is certain to be intermediate between the potentials of reactions (4) and (10). Moreover, Shoesmith et al.[19] reported that $NaFeS_2$ was formed at potentials in the vicinity of peak IA, which helps to substantiate the formation of FeS_2^- at this potential.

Beyond peak IA, FeS_2 or FeS_2^- could be oxidized to FeOOH or Fe_2O_3, which could be responsible for the onset of passivity at potentials above peak IA.

$$FeS_2 + 5H_2O \longrightarrow FeOOH + S_2O_3^{--} + 9H^+ + 7e^- \quad (12)$$

$$2FeS_2 + 9H_2O \longrightarrow Fe_2O_3 + 2S_2O_3^{--} + 18H^+ + 14e^- \quad (13)$$

According to Tromans,[15] these films appear to be protective and inhibit continued metal dissolution at potentials above peak IA.

Cathodic Reactions

Direct reduction of thiosulfate ions via Equations 14 or 15 appears to be kinetically limited on gold electrodes, as shown in Figure 4.

$$S_2O_3^{--} + 8H^+ + 8e^- \longrightarrow 2HS^- + 3H_2O \quad (14)$$

$$S_2O_3^{--} + 8H_2O + 8e^- \longrightarrow 2HS^- + 8OH^- + 3H_2O \quad (15)$$

The cathodic scans on gold electrodes are consistent with an initial reduction of polysulfide ions at more noble potentials, followed by hydrogen ion reduction when the applied potential falls below the hydrogen half-cell potential. Only minor changes in the cathodic current densities were observed in cathodic scans on the gold electrodes over thiosulfate concentrations ranging from 0 to 25 g/L. Small changes could be explained by small changes in the polysulfide concentration associated with thiosulfate disproportionation.

On the steel electrodes, however, an increase in cathodic current density was observed with increasing thiosulfate concentration. Furthermore, the cathodic polarization curves did not exhibit the characteristic concentration polarization associated with polysulfide reduction, as found on the gold electrodes. These observations suggest that another species — presumably thiosulfate — is being reduced directly on the carbon steel electrode surface, in contrast to the behavior on gold surfaces.

Although there may be many possible explanations for differences in

cathodic behavior on gold and steel electrodes, a plausible explanation is that reaction (14) is stimulated on steel surfaces because of the availability of hydrogen ions derived from reactions (4-6,8-10, 12,13). Hydrogen ions are liberated in these reactions associated with the dissolution of iron from the steel electrodes. These hydrogen ions are then available for reaction (14), but only on the surface of the steel electrode. On gold, there is no production of hydrogen ions via these corrosion reactions. The high pH restricts the supply of hydrogen ions at the gold electrode surface and reaction (14) does not proceed. The reasons for kinetic limitations on the alternative thiosulfate reduction — reaction (15) — are unknown.

Alternatively, the presence of iron sulfide deposits on the steel electrodes may catalyze the thiosulfate reduction reaction, thereby eliminating the high overvoltages associated with reactions (14-15) on the inert gold electrode surface.

The reduction of thiosulfate via reactions (14-15) may also generate additional HS^- ions in close proximity to the corroding steel surface. These HS^- ions can then react with the steel surface via reaction (4), thereby offsetting any concentration polarization effects associated with HS^- consumption via this reaction.

Thus, the apparent role of thiosulfate reduction in the corrosion of carbon steel is to consume electrons liberated in the dissolution reaction and perhaps to replenish HS^- at the electrode surface.

In the absence of thiosulfate, the only reduction reactions available to support iron dissolution are trace polysulfide reduction and hydrogen reduction (at potentials below the hydrogen half-cell potential). The polysulfide reduction reaction will only support modest corrosion rates, since the diffusion-limited current densities for polysulfide reduction (on gold) are approximately 3×10^{-2} mA/cm^2. If this current density represents an upper limit to the cathodic current density on iron surfaces, it corresponds to a corrosion rate of approximately 20 mils per year, assuming ferrous ion production. Higher corrosion rates in the absence of thiosulfate must involve hydrogen reduction in the cathodic process. However, the close proximity of the hydrogen reduction potential to the ferrous ion dissolution potential will prevent corrosion rates much in excess of 20 mils per year unless thiosulfate reduction is involved.

When thiosulfates are not present in the synthetic liquors, the corrosion product expected on corroding steel surfaces is either stoichiometric FeS (troilite) or mackinawite (Fe_9S_8) associated with reaction (4). In the absence of stronger oxidants than trace polysulfides, higher sulfides (generated by reaction 10, for example) are not expected. This agrees with the observation of Fe_9S_8 as the principal corrosion product for specimens exposed to solutions with a low thiosulfate concentration.

When corrosion occurs on steels exposed to thiosulfates, the overvoltage for thiosulfate reduction is apparently reduced and thiosulfate becomes an oxidant that can stabilize higher sulfides as reaction products. In particular, it appears that the corrosion of plain carbon steel in liquors containing thiosulfates produces a soluble FeS_2^- species as the principal corrosion product. The FeS_2^- species eventually precipitates as polymeric $NaFeS_2$ on all wetted surfaces. However, it does not appear that the $NaFeS_2$ deposits are very protective, since very high corrosion rates are observed in their presence.

In synthetic liquors without thiosulfates, the only species which can oxidize corrosion products to form higher sulfides are trace quantities of polysulfides. Consequently, the corrosion products formed in liquors devoid of thiosulfate are devoid of significant quantities of higher sulfides or $NaFeS_2$.

The oxidizing nature of the thiosulfates when in contact with corroding

steel surfaces explains the higher rest potentials observed in liquors with high thiosulfate concentrations. These higher potentials coincide with the production of FeS_2^- as the principal corrosion product.

The rate of corrosion in solutions with intermediate thiosulfate concentrations was generally lower than the rates observed in liquors with higher or lower thiosulfate concentrations. This reduction in the corrosion rate is not associated with complete passivation of the carbon steel, which occurs at higher potentials associated with formation of Fe_2O_3. The rate of corrosion may be reduced due to formation of a surface film that is more protective than the Fe_9S_8 deposit, and much more protective than the $NaFeS_2$ film that forms at still higher potentials. This protective film that forms at intermediate potentials may be associated with formation of magnetite via reactions 5-7, which is stabilized in this potential regime.

Thus, four ranges of potential have been identified as follows:

I. Zone 1. (-230 to - 215 mVSSSE)

Moderate corrosion rates, Fe_9S_8 corrosion product, low thiosulfate concentrations, trace polysulfide and some hydrogen reduction.

II. Zone 2. (-215 to -125 mVSSSE)

Lower corrosion rates, moderate thiosulfate concentrations, some thiosulfate reduction, likely formation of protective magnetite films.

III. Zone 3. (-125 to -30 mVSSSE)

Very high corrosion rates, significant thiosulfate reduction, FeS_2 production with precipitation of nonprotective $NaFeS_2$ deposits.

IV. Zone 4.(above -30 mVSSE)

Very low corrosion rates. Passivation by formation of Fe_2O_3. Oxidation of HS^- to polysulfide.

Liquor Composition Changes. Liquor analyses revealed consistent changes in composition as a result of corrosion of the carbon steel coupons. The sulfide concentration decreased during corrosion, apparently due to consumption of HS^- in the oxidation of iron to Fe_9S_8 or FeS_2^-. The thiosulfate concentration decreased only slightly, however, apparently because of reduction processes on the steel surfaces. Some oxidation of sulfides through inadvertent contact with air may have offset this loss of thiosulfate.

The sulfite concentration decreased significantly in all of the liquors, with the largest reductions observed in the most corrosive liquors. If the thiosulfate concentration is decreased by reduction reactions, and sulfides are incorporated in corrosion product films, the sulfite concentration would also be reduced via the equilibrium reaction (1). The loss of sulfite would be greatest in liquors where thiosulfate reduction supports very high corrosion rates, as was observed.

The polysulfide concentration in the liquors remained essentially constant and very low (0.01 g/L) during the corrosion studies. Polysulfide alone could not provide the levels of the cathodic reduction required to support the corrosion rates observed in some of the synthetic liquors.

Corrosion Mechanism

All of the results discussed above are consistent with the following mechanism of corrosion in synthetic white liquors containing high concentrations of thiosulfates. Iron oxidation to FeS_2^- occurs in two steps, via reaction (4) followed by reaction (11). The protons and electrons liberated in these reactions will be consumed by direct reduction of thiosulfate via reaction (14). The FeS_2^- species is soluble at the surface of the steel but eventually precipitates in the bulk solution and on wetted surfaces as a nonprotective $NaFeS_2$ compound.

CONCLUSIONS

The following conclusions are drawn from this investigation.

1. The rate of corrosion of carbon steel exposed to synthetic kraft white liquors is increased significantly by high concentrations of thiosulfate in the liquor.

2. Accelerated corrosion induced by thiosulfates is accompanied by increased rest potentials and the formation of $NaFeS_2$ compounds.

3. Thiosulfate reduction occurs on carbon steel electrodes exposed to kraft liquors but does not occur to a significant extent on noble metal electrodes.

4. Accelerated corrosion induced by thiosulfates cannot be attributed to the decomposition of thiosulfate to form polysulfides.

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TABLE 1

SUMMARY OF COUPON EXPOSURE TESTS

Target Thiosulfate	Average Corrosion Rate, mpy	Time	Composition, g/L						Final ϕ,** mVSSSE
			NaOH	Na_2S	$Na_2S_2O_3$	Na_2SO_3	Na_2SO_4	Na_2S_2	
0	11	I	100	35	2.7	6.3	1.2	<0.01	-210
		F	102	31	3.6	6.1	0.4	0.04	
2	33	I	100	38	5.8	4.3	1.1	<0.01	-200
		F	105	31	6.8	5.2	0.7	0.03	
4	19	I	101	33	7.6	6.0	1.1	<0.01	-140
		F	104	30	8.3	5.5	0.8	<0.01	
6	19	I	97	30	10.0	4.5	1.1	<0.01	-140
		F	99	30	12.5	4.8	0.4	<0.01	
8	23	I	100	31	13.0	6.5	1.4	0.05	-145
		F	104	28	18.6	5.2	0.6	<0.01	
10	32	I	101	31	15.1	4.2	1.2	0.14	-125
		F	104	29	21.0	4.3	0.8	<0.01	
12	89	I	101	33	16.7	6.6	0.9	0.02	-110
		F	104	28	21.6	4.4	0.7	0.02	
16	71	I	102	33	21.3	7.8	0.9	0.03	-110
		F	105	28	27.1	4.0	0.5	0.02	
20	53	I	101	34	25.4	5.4	1.1	0.40	-120
		F	104	30	33	4.9	0.6	0.03	
25	74	I	99	32	29.8	5.2	1.0	0.10	-30
		F	104	25	45.1	3.1	0.8	<0.01	
0*	23	I	100	33	1.8	3.7	0.4	<0.01	
		F	105	24	0.3	4.6	0.2	<0.01	

I = Before testing.
F = After testing.
* Liquor prepared by H_2S reaction in Na_2S.
**In general, potentials increased during exposure and average potentials would be lower by 10-30 mV.

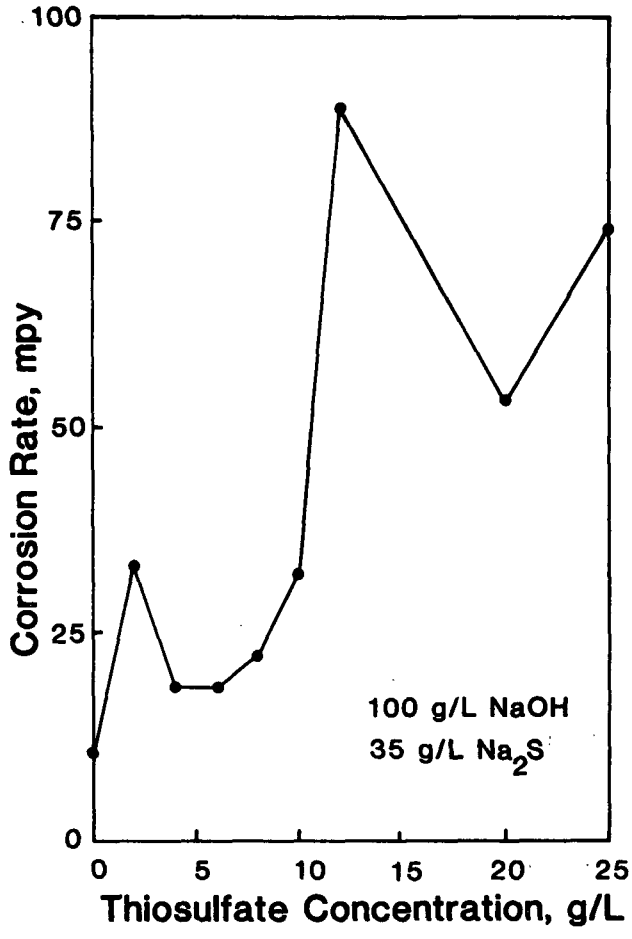

FIGURE 1--Effect of thiosulfate on corrosion of carbon steel by white liquor

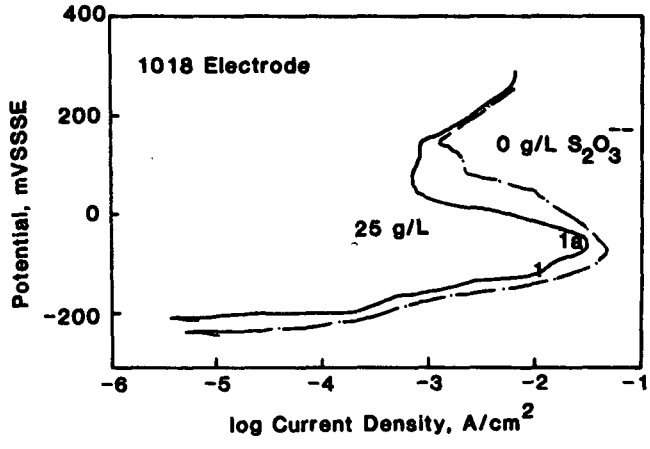

FIGURE 2--Representative anodic polarization curves for carbon steel exposed to white liquors containing high and low thiosulfate levels.

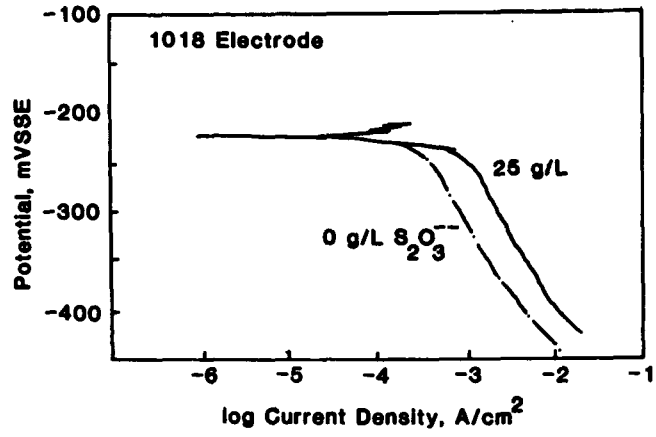

FIGURE 3--Representative cathodic polarization curves for carbon steel exposed to white liquors containing high and low thiosulfate levels.

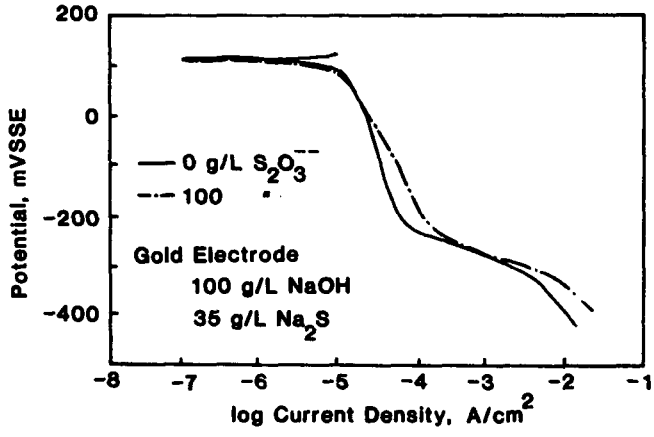

FIGURE 4--Representative cathodic polarization curves for gold exposed to white liquor containing high and low thiosulfate levels.